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# The Crystalline Structure of Ethylene-Butene-1 Copolymers

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Random copolymers of ethylene and butene-1, which covered a very wide range in the composition ratio between the two monomers, were synthesized by copolymerization with organo-metallic compound catalysts,  $\text{VOCl}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ . The crystalline structure of those copolymers crystallized from the melt and solution was studied with the aid of x-ray diffraction, infrared absorption, differential thermal analysis techniques and electron microscopic observation. It was confirmed that when they were supercooled from the melt the two comonomer units were not able to cocrystallize in accord with the conclusion which had been demonstrated by various investigators,<sup>1,2,3,4)</sup> but when supercooled from the solution an evidence was obtained that the comonomer units could crystallize in common crystalline lattices. This result is interpreted morphologically in relation to the fact that the crystalline forms of the homopolymers synthesized from the two monomers, polyethylene as well as isotactic polybutene-1, are both orthorhombic when crystallized from the solution, while that of the latter is not orthorhombic when crystallized from the melt.

## INTRODUCTION

It has been firmly demonstrated from thermodynamical studies<sup>1,2,3)</sup> that, in copolymers whose major chain units are methylene  $\text{-CH}_2\text{-}$ , propylene units  $\begin{array}{c} \text{-CH-} \\ | \\ \text{C}_2\text{H}_5 \end{array}$  could not be incorporated in the crystalline lattice composed of methylene units when the copolymers are supercooled from the melt, although some inconsistency still persists between the investigators<sup>1,2,3,4)</sup> as to whether copolymerizing units such as ethylene unit  $\begin{array}{c} \text{-CH-} \\ | \\ \text{CH}_3 \end{array}$  smaller than propylene unit can be incorporated or not. This result should be very plausible also in view of morphological studies of the copolymers, because the crystalline form and crystallographic parameters of linear polyethylene  $\text{-(CH}_2\text{-CH}_2\text{)}_n\text{-}$  and those of isotactic polybutene-1  $\text{-(}\begin{array}{c} \text{CH}_2\text{-CH} \\ | \\ \text{C}_2\text{H}_5 \end{array}\text{)}_n\text{-}$  are quite different each other such as the crystalline form of the former is orthorhombic and that of the later is not orthorhombic but hexagonal or tetragonal, if those homopolymers are crystallized from the melt. However, if they are super-

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cooled from the solution, the situation becomes to be somewhat different.

Linear polyethylene generally exhibits a very stable orthorhombic crystalline form even though supercooled from the solution in a similar way as when supercooled from the melt. On the contrary, isotactic polybutene-1 exhibits different crystalline forms including orthorhombic one depending on the crystallization condition. Its orthorhombic form hardly could be produced except on a limited condition of the crystallization from the solution, but it is not so stable as either crystalline forms.<sup>5)</sup> However, it has been pointed out<sup>6)</sup> that in some kinds of olefin copolymers, if the crystalline forms of homopolymers from each component monomer are the same, the occurrence of isomorphous replacements between two kinds of monomer unit in the crystalline structure of the copolymers could be expected so that the so-called isomorphism or isodimorphism phenomena of crystallization took place even though the crystallographic parameters of each homopolymer are little different each other. Hence, even in copolymers of ethylene and butene-1 in the present case if they are supercooled from the solution under such proper condition that both homopolymers from the two monomers can be crystallized in orthorhombic forms, possibility that some numbers of methylene unit in the crystalline phase of the copolymers are isomorphously replaced with propylene units and as the result the copolymers can exhibit a high level of crystallinity in some range of the composition, should not be ignored without examination. We will examine the crystalline structure of the copolymers which are crystallized under various conditions in view of these consideration.

## EXPERIMENTAL

**Copolymerization.** It was desirable in this work to use copolymers whose compositions were as uniform as possible and both comonomer units, ethylene and butene-1, were distributed at random in the molecular chains. Kelly et al.<sup>7)</sup> reported that copolymers of ethylene and propylene, both comonomers of which are distributed at random could be synthesized by using the soluble homogeneous catalytic system composed of aluminium alkyl chloride and trichloroxyvanadium. On the other hand, it is recognized that this catalytic system is non-stereospecific for homopolymerization of propylene. But although this catalytic system  $\text{VOCl}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  had not been adopted as yet for polymerizations of butene-1, it was found in this study that this system was capable of producing isotactic polybutene-1. We tried the copolymerization of butene-1 and ethylene with this catalytic system and as the result random copolymers could be obtained. The experimental detail is as follows. Since it was expected that the reactivity of ethylene was generally much higher than that of butene-1 in anionic copolymerizations,<sup>8)</sup> continuous addition of mixing gas of both comonomers to the polymerization system was needed to prevent the production of homopolymers. So far the catalytic system and composition of reaction mixtures are the same, the composition of the resulting copolymer is inferred to be independent of (1) the concentration of the catalytic system, (2) the time elapsed between the preparation and use of it, (3) the polymerization time and the relative molar ratio of aluminium to vanadium in the catalytic system. In homopolymerizations of each comonomer, if the molar

ratio of Al to V was less than 5, the intrinsic viscosity number of homopolymers produced was very low, though it was so increased with raising the ratio from 5 to 10 that homopolymers having a relatively high viscosity number could be obtained. Hence, in copolymerization with this catalytic system 7.5 was utilized as the molar ratio of Al to V to prepare copolymers of high molecular weight.

Into a 1 liter flask previously replaced with nitrogen gas, were added 300 ml. of monochlorobenzene as a diluent and 0.5 ml. of trichloroxyvanadium and 5 ml. of diethyl aluminium chloride as catalysts at room temperature. After the temperature of the mixture was slowly elevated to the reaction temperature of 30°C under stirring, the mixture of ethylene and butene-1 of a predetermined composition was introduced into the flask continuously through a gasmeter. The reaction was stopped by putting the reactant into a large amount of isopropyl alcohol, and pouring large amount of mixture of methanol and hydrochloric acid. The solid polymer was precipitated for 24 hours and purified by washing repeatedly with hot methanol. The composition of the copolymers thus obtained was determined with the ratio of two absorbances of the infrared bands at 762 cm<sup>-1</sup> for butene-1 components and 720 cm<sup>-1</sup> for ethylene components. For this purpose, the relation between the ratio of the two absorbances and mixing ratio in the mixture of two homopolymers from each monomer was previously established. Utilizing this relation, the composition of copolymers was estimated. The infrared measurement was carried out with films of each sample by a Hitachi EPI-510 infrared spectrophotometer. Furthermore, to estimate ethyl contents of copolymers a technique developed by Terahashi and Sugahara was also used.<sup>9)</sup>

The distribution of the comonomer components in the copolymers was investigated as described in a later section. The copolymers thus prepared were used for further studies as well as homopolymers polymerized with the same catalytic system.

**Crystallization of samples.** The copolymers and homopolymers thus obtained were crystallized from melt or from solution. For the crystallization from melt in x-ray and infrared spectrum studies, the specimens were first allowed to completely melt at 150°C for several hours and molded into a film of about 0.2 mm. thick at that temperature and cooled slowly to room temperature at the rate of 6°C/hour. For the study of differential thermal analysis, the specimens were crystallized in the same way in vacuum and crushed into powder states. The crystallization from the solution of the samples was also carried out, and its detail will be described in the section of the electron microscopic observation technique.

**Crystallinity.** The degree of crystallinities of the bulk crystallized specimens was estimated by the density and x-ray techniques. The densities of the film samples crystallized from melt as described in the foregoing section were estimated with the density gradient column composed of ethylene glycol and *n*-propyl alcohol at 30°C. The density thus obtained was converted to the degree of crystallinity by the relation,

$$X_d = \frac{\{(1 - W_e)V_{a,b} + W_e V_{a,e}\} - V_{obs.}}{V_{a,b} - V_{c,e}}$$

Here,  $V_{obs.}$  is the observed specific volume of the sample,  $V_{a,e}$  and  $V_{a,b}$  are the

specific volumes of the completely amorphous polyethylene and polybutene-1 respectively at 30°C, which are 1.173 cm<sup>3</sup>/g. and 1.205 cm<sup>3</sup>/g., and  $V_c$  is that of completely crystalline polyethylene, the value of which is 1.003 cm<sup>3</sup>/g.  $W_e$  is the mass fraction of ethylene components in copolymers. The crystallinities from x-ray study are calculated in a similar manner which was used by us for copolymers of butene-1 and 4-methyl-1-pentene and others<sup>10</sup>.

**Differential thermal analysis.** A conventional apparatus for differential thermal analysis, DT-IOB type, manufactured by Shimazu Seisakusho Ltd., was used. About 100 mg. of powder samples crystallized from the melt as described above were inserted into the platinum cell of the apparatus. Fused silica powder was used as the reference material. The sample was heated at the rate of 10°C/min. under atmospheric surroundings.

**Extraction of copolymers with *n*-heptane.** To examine the distribution of the molecular composition in copolymers extraction was carried out with *n*-heptane. Linear polyethylene is generally insoluble in *n*-heptane even at elevated temperature, while isotactic polybutene-1 is soluble in it. Hence, the extraction with *n*-heptane was conducted for the copolymers for the purpose mentioned above.

**Electron microscopic observation of the solution crystallized samples.** *p*-Xylene solution of 0.1 % of the specimens was prepared at 140°C and then transferred to a thermostat bath of 80°C and this temperature was hold over 24 hours. Through this procedure the polymers were separated from the mother solution in a suspended state. The suspended material was next removed with a glass rod and deposited directly onto electron microscopic grids coated with polyvinyl formal films. The grids were reinforced with carbon and shadowed with chromium at an angle of 30°.

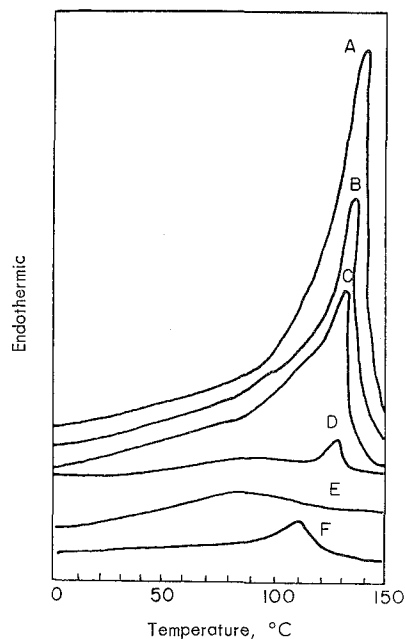
## RESULTS AND DISCUSSION

**Characterization of ethylene and butene-1 copolymer.** Some properties of copolymers studied are summarized in Table 1. As Barral<sup>11</sup> pointed out on the characterization of copolymers of ethylene and propylene, a differential thermal analysis method can aid in obtaining informations of whether the copolymers are random or block. In the thermal curves of a block copolymer or mixture of homopolymers, there can generally be found two peaks, corresponding with the respective components. On the other hand, in random copolymers there is generally observed only one endothermal peak or no peak can be revealed for copolymers in a medium range of copolymerizing ratio. In Fig. 1 are illustrated the differential thermograms for ethylene-butene-1 copolymers with various compositions. As expected for polyethylene, only one endothermal peak is recognized in the vicinity of 140°C corresponding to its melting. For copolymers, this endothermal peak caused by the melting of ethylene components is shifted to lower temperatures and the area thereof diminishes as butene-1 contents increase, but no peaks more than two could be observed by all means. The copolymers of higher contents of butene-1 such as 67.5 mole-% never reveal any peak in the thermogram. Therefore, it may be supposed that the copolymerized products studied should be neither

Table 1. Copolymerization of ethylene and butene-1  
 $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VOCl}_3=7.5$  in molar ratio;  $\text{VOCl}_3$ ,  $5.28 \times 10^{-3}$  mol; Solvent, Chlorobenzene 400 ml.; Reaction temperature,  $30^\circ\text{C}$ ; Pressure, 1atm.

Experimental No.	Butene-1 composition* in copolymer, mole-%	Density at $30^\circ\text{C}$ g/cc.	Temperature at peak in differential thermograms, $^\circ\text{C}$
Polyethylene	0	0.942	140
Copolymer 1	0.54	0.924	133
2	3.2	0.922	128
3	8.4	0.915	127
4	19.5	0.912	125
5	21.0	0.911	125
6	34.0	0.872	124
7	50.0	0.851	123
8	54.0	0.842	122
9	55	0.840	122
10	67.5	0.840	—
11	98.4	0.855	100
Polybutene-1	100	0.860	104

\* Estimated by infrared techniques



A, Polyethylene  
 B, Copolymer (Butene-1=3.2 mole-%)  
 C, 21.0  
 D, 34.0  
 E, 67.5  
 F, Polybutene-1

Fig. 1 Differential thermograms of homo- and copolymers of ethylene and butene-1

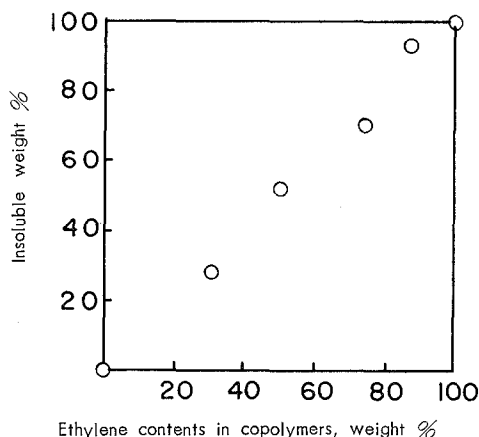


Fig. 2 Solvent extraction of copolymers of ethylene and butene-1

mixtures nor block copolymers of two monomers but random copolymers.

In addition, in Fig. 2 the insoluble fractions of the copolymers in boiling *n*-heptane are plotted against the weight fraction of ethylene contents. It is easily ascertained from the results that the weight fractions of ethylene components are almost equal to the insoluble fractions over the whole composition range of copolymerization. Hence, the supposition made above that the copolymerized products are random copolymers will be further confirmed. Furthermore, it may be inferred from considering the above results as well as the properties of polymerization catalysts that both copolymerizing units are distributed uniformly in copolymeric chains.

**Crystallinity of copolymers crystallized from the melt.** The level of crystallinity of the copolymers estimated by the x-ray technique and density measurement is plotted against their composition in Fig. 3, where the polymers have been supercooled from the melt. It is recognized from the figure that the crystallinity rather abruptly decreases with incorporating of a small amount of comonomer

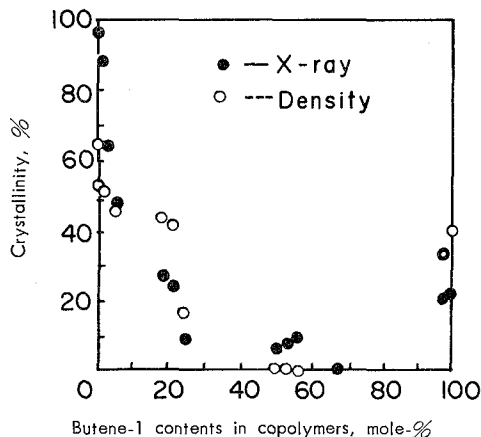


Fig. 3 Crystallinity of ethylene-butene-1 copolymers estimated by x-ray and density against butene-1 contents

into copolymeric chains, and that for the copolymers with the high butene-1 contents such as 70-80mole-%, no crystallinity is indicated. Hence, in this case where the copolymers have been supercooled from the melt, it is concluded as expected<sup>1,2,3,4)</sup> that neither cocrystallization nor isomorphism can occur between two comonomer units in copolymeric chains.

**Electron microscopic observation of copolymers crystallized from the solution.**

A large number of studies has been made on the crystalline structure of linear polyethylene crystallized from the solution.<sup>12)</sup> The coincident conclusion reached by these investigations is that if linear polyethylene is crystallized from the solution, using proper solvents such as *p*-xylene and conditions, the so-called single crystal could be produced, the crystal form of which is orthorhombic similar as crystallized isothermally from the melt in a temperature range close to the melting temperature. On the other hand, for isotactic polybutene-1 the situation is a little complicated so that the formation of single crystal and the crystalline form thereof depend on the sort of solvent used and condition under which the crystallization is conducted.

Holland and Miller<sup>5)</sup> obtained the single crystal of polybutene-1 by the isothermal crystallization at 58°C from the amyl acetate solution, and assigned its crystalline form to be orthorhombic, which was called Form III by them. Furthermore, Reneker<sup>13)</sup> obtained the similar result, using *p*-xylene as solvents. Thus, linear polyethylene as well as isotactic polybutene-1 should crystallize in orthorhombic form, if they were supercooled from the solution under proper conditions. Hence, if copolymers of ethylene and butene-1 are supercooled from the *p*-xylene solution under the condition that the orthorhombic crystalline forms can be produced from both homopolymers, the occurrence of cocrystallization or isomorphism phenomena between two monomer units in the copolymeric chains might be presumed, despite that the crystallographic parameters of two homopolymers are somewhat different each other, *a*- and *b*-axes of crystal unit cells are 7.4 and 4.9 Å for polyethylene and 12.49 and 8.96 Å respectively for polybutene-1 and the crystalline form of the latter is not stable as that of the former.

According to the techniques described in the experimental section, the copolymers crystallized from the *p*-xylene solution were observed by an electron microscope. The electron microscopic photographs are depicted in Fig. 4. As can be seen, the single crystal of rhombic or oval shape according to the composition of samples can clearly be observed. In observing single crystal of the copolymers, all copolymer fractions which had been separated from the *p*-xylene solution by the technique described in the experimental section did not necessarily exhibit such single crystal forms as indicated in Fig. 4. Hence, a question still could reside in whether the observed single crystals were formed with the copolymer fractions which corresponded to the copolymerizing composition of the total system or not. However, it should be interesting to note that the results obtained here may suggest the possibility of occurrence of the isomorphism between methylene and propylene units if the copolymers are supercooled from the solution.



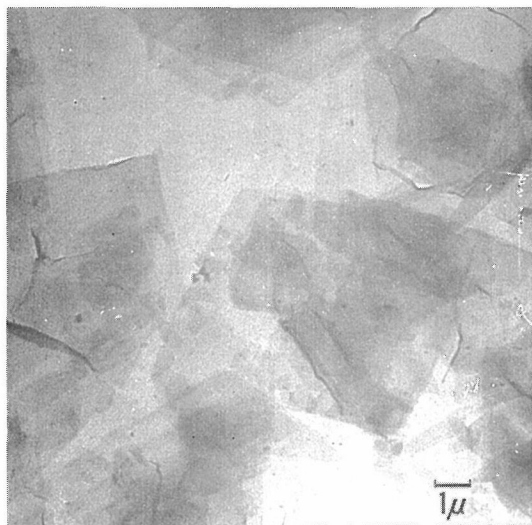


Fig 4-1 Crystals of linear polyethylene crystallized from p-xylene solution



Fig. 4-2 Crystals of copolymer of ethylene and butene-1 (Sample; Copolymer 2 in Table 1).  
Some fractionation may be occurred during crystallization.

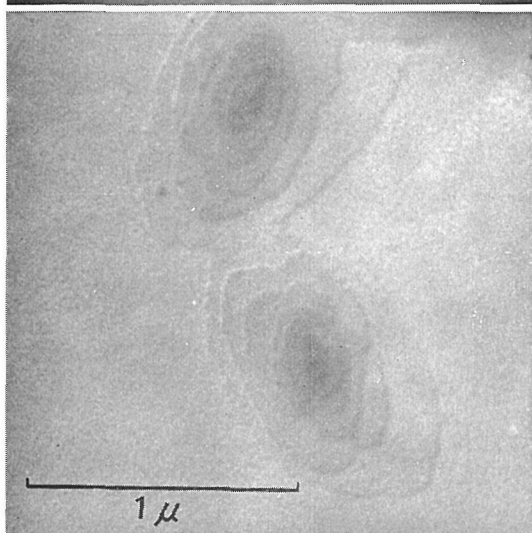


Fig. 4-3 Crystals of copolymer of ethylene and butene-1 (Sample; Copolymer 4 in Table 1)

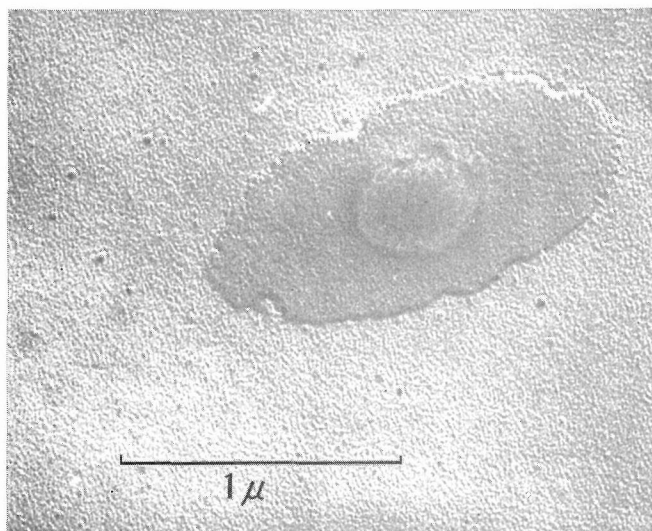


Fig. 4-4 Crystals of copolymer of ethylene and butene-1 (Sample; Copolymer 6).

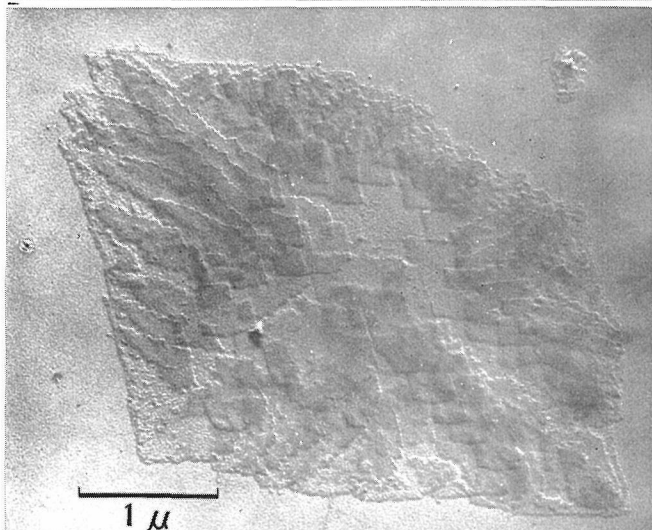


Fig. 4-5 Crystals of copolymer of ethylene and butene-1 (Sample; Copolymer 11).

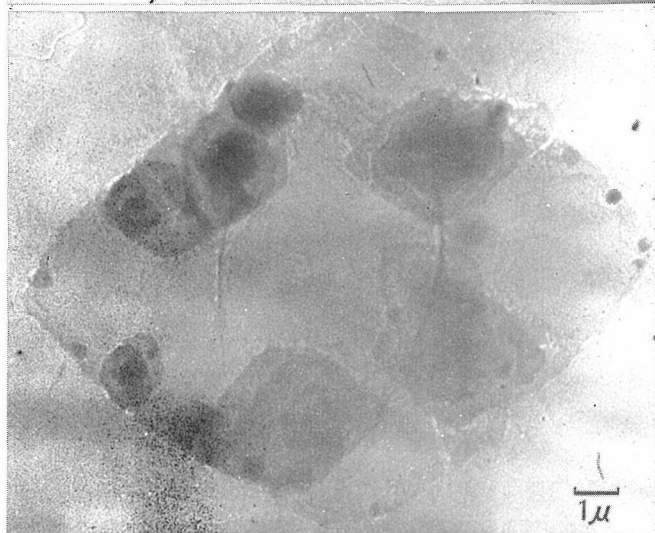


Fig. 4-6 Crystals of isotactic polybutene-1 crystallized at 80°C from p-xylene solution.

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